

**ADSORPTION PHYSICS OF METALS PARTIALLY COVERED  
BY METALLIC PARTICLES. II  
DESORPTION RATES OF ATOMS AND IONS**

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Received 26 November 1963

Desorption rates of atoms and ions from metallic surfaces immersed in a monatomic metallic vapor are calculated theoretically. The calculations are based on the assumptions that the adsorbed vapor particles consist of a single species held onto the surface by bonds that are partially ionic and partially covalent. The rates are derived from a statistical mechanics formalism pertaining to the surface and vapor phases of the system.

The theoretical results are shown to be in good agreement with available experimental data.

The same statistical mechanics formalism is extended to the problem of vaporization and sublimation from pure surfaces. Good agreement between theory and experiment is established. The purpose of this extension is to indicate the internal consistency of the approach by availing the theoretical results with more experimental data for comparison.

A unique feature of the derived formulas is that they do not involve adjustable constants.

### **1. Introduction**

In previous analyses the authors presented theoretical calculations of the electron work function<sup>1)</sup> and the desorption energies of atoms and ions<sup>2)</sup> by extending concepts of molecular physics to adsorption physics. In the present communication, part II of a series of three papers, the desorption rates of atoms and ions are calculated theoretically by using the previous analyses together with a well established statistical mechanics rate formalism. The derived rates are used in part III to set up an equation of state for composite surfaces and to compute electron emission *S*-curves.

The present communication is organized as follows. First, an outline of the surface system and the desorption problem under discussion is given. Second, a brief review of previous theoretical approaches to the problem is presented. Third, desorption rates of atoms and ions are derived theoretically. Finally,

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the derived correlations are compared with available experimental results and good agreement between theory and experiment is established.

A unique feature of the derived theoretical correlations is that they do not involve adjustable constants.

The study is applicable only to metallic surfaces immersed in monatomic metallic vapors. This restriction results in some both simplifying and practical features of the problem which are not present in other adsorption systems, as discussed in ref. <sup>2</sup>).

## 2. Desorption rates from composite surfaces

### 2.1. GENERAL REMARKS AND BRIEF LITERATURE REVIEW

The adsorption system under consideration is a pure metallic surface at temperature  $T$  immersed in a metallic vapor bath at temperature  $T'$ . When dynamic equilibrium is established, a fraction  $\theta$  of the surface is covered by adsorbed particles. Nucleation or clumping is not presumed to occur because  $T > T'$ .

The desorption rates,  $E_a$  of atoms or  $E_p$  of ions, are in general explicit functions of  $\theta$  and  $T$ . Also, they may be implicitly dependent on  $T$  through the small thermal expansions of the substrate lattice parameters, but this dependence is usually considered a second order effect and is neglected.

For the theoretical correlation of experimental results, many investigators use the Arrhenius form of the rate equation:

$$E_i = c_i \exp(-\phi_i/kT) \quad (1)$$

where  $c_i$  is the Arrhenius coefficient,  $\phi_i$  is the desorption energy of the  $i^{\text{th}}$  species and  $k$  is the Boltzmann constant. Thus, the theoretical efforts are devoted to the evaluation of  $c_i$  and  $\phi_i$ . The calculation of  $\phi_i$  has been discussed elsewhere <sup>2</sup>).

Regarding  $c_i$ , different workers propose a variety of techniques for its calculation. De Boer <sup>3</sup>), Tompkins <sup>4</sup>) and Warner <sup>5</sup>) use a statistical mechanics surface model but do not succeed in expressing  $c_i$  without arbitrarily adjustable functions. Becker <sup>6</sup>) uses an arbitrary formula without any justification. Taylor and Langmuir <sup>7</sup>) determine theoretically a trend in the dependence of  $c_i$  on the coverage  $\theta$  ( $c_i$  is a strongly varying function of  $\theta$ ) but they compute  $c_i$  by empirically fitting experimental atom emission data for Cs on W. Rasor <sup>8</sup>) uses the Taylor-Langmuir data for Cs and W and a semi-empirical approach to infer  $c_i$  for other composite surfaces. Laidler <sup>9</sup>), Higuchi, Ree and Eyring <sup>10</sup>), Moore and Allison <sup>11</sup>), Zingerman <sup>12</sup>), and many other investigators use the transition state approach to the problem. This approach is somewhat similar to the statistical mechanics approach mentioned above

but it requires the existence and the postulated properties of a transition state located at a hump in a surface potential energy profile. For metallic particles adsorbed on metallic surfaces, however, such a hump cannot exist because it is found experimentally that the rate of incidence of vapor particles is equal to the rate of adsorption. In addition, the postulated properties of the proposed unstable transition state are questionable.

It is felt that a statistical mechanics surface model in conjunction with the assumption that the vapor particles are chemisorbed on the surface as a single, mobile, vibrating, species, are adequate to provide the means for the complete theoretical evaluation of the desorption rates without adjustable constants.

## 2.2. STATISTICAL MECHANICS FORMALISM FOR COMPOSITE SURFACES

For clarity in setting up a statistical mechanics formalism for composite surfaces, consider first a thermodynamic system consisting of two phases only, the vapor phase and the surface phase, in thermal equilibrium at a temperature  $T$ . The number of vapor particles of the  $i^{\text{th}}$  species is  $n_i$  and the total vapor volume is  $V$ ; the number of adsorbed particles is  $N$  and the total surface area for adsorption is  $A_s$ . The adsorbed particles are assumed to be of one hybrid species held onto the surface by bonds which are partially ionic and partially covalent.

If it is assumed that the adsorbed particles have two degrees of translational freedom parallel to and one degree of vibrational freedom perpendicular to the surface, then the partition function  $Q$  is:<sup>13)</sup>

$$Q = \prod_{i=1} \left[ \frac{\omega_i (2\pi m_f kT)^{\frac{3}{2}} V}{h^3} \exp(-\Phi_i/kT) \right]^{n_i} \frac{1}{n_i!} \times \left[ \frac{2\pi m_f kT A_f}{h^2} \cdot \frac{kT}{h\nu_1} \exp(-\Phi_N/kT) \right]^N \frac{1}{N!}, \quad (2)$$

where  $m_f$  is the mass of the adsorbed film particles,  $\omega_i$  is the statistical weight of the  $i^{\text{th}}$  species of vapor particles\*,  $\Phi_i$  and  $\Phi_N$  are the potential energies of the corresponding vapor and surface particles, respectively, referred to an arbitrary zero potential,  $\nu_1$  is the vibration frequency\*\*,  $A_f$  is the free area available for translation (which is shown later to be less than the total area  $A_s$ ), and  $h$  is Planck's constant. The quantities  $\Phi_N$ ,  $\nu_1$  and  $A_f$  are generally

\* The statistical weight of the surface particles is identically equal to unity because electron spins are always paired in chemical bonds<sup>14</sup>.

\*\* The vibrational frequency is calculated to be usually of the order of  $10^{12} \text{ sec}^{-1}$ . Thus, the rigorous partition function for vibration,  $(1 - \exp(-h\nu_1/kT))^{-1}$ , can be adequately approximated by  $kT = h\nu_1$ , above room temperature.

functions of  $N$  and  $T$ . However, if thermal expansions are neglected these quantities may be considered as functions of  $N$  alone<sup>15</sup>). The  $\prod_i$  is taken over all atomic, ionic and excited species of vapor particles. Only one hybrid surface species need be considered in the product, however, because of the complete quantum mechanical overlapping of excited state bonds in inter-metallic compounds<sup>2</sup>).

The mobile model of the adsorbed particles is consistent with the previous work on electron work function<sup>1</sup>) and the experimental fact that for all coverages all incident particles are adsorbed and none reflected. The differences in numerical results arising from assuming mobile or immobile surface particles are discussed later in the paper.

By equating the surface and vapor phase chemical potentials derivable from eq. (2), it is found that:

$$(n_i/V)(kT/2\pi m_i)^{\frac{1}{2}} = \omega_i \sigma_f \theta v \exp(\Delta S/k) \exp(-\phi_i/kT), (\text{cm}^{-2} \text{sec}^{-1}) \quad (3)$$

where the following new definitions have been introduced:

$\theta \equiv$  fraction of surface coverage,

$\sigma_f \equiv$  adsorbate surface density at  $\theta = 1$ , ( $\text{cm}^{-2}$ )

$\sigma_f \theta \equiv N/A_s$ , ( $\text{cm}^{-2}$ )

$v \equiv v_1 \exp[(\theta \partial \ln v_1 / \partial \theta)]$ , ( $\text{sec}^{-1}$ )

$\exp(\Delta S/k) \equiv (A_i/A_f) \cdot \exp[\theta \partial \ln(A_i/A_f) / \partial \theta]$ ,

$\phi_i \equiv \Phi_i - \Phi_N - \theta \partial \Phi_N / \partial \theta$ , (eV).

$v$  is an effective frequency;  $\Delta S$  is interpreted later to be a configuration entropy difference, and  $\phi_i$  is the *potential energy* with respect to the ground state of the surface. In essence, the potential energy  $\phi_i$  is the desorption energy of the  $i^{\text{th}}$  species and it contains the term  $(\theta \partial \Phi_N / \partial \theta)$  because the removal of one particle alters the potential energy of the other particles.

The left hand side term of eq. (3) is the arrival rate of the  $i^{\text{th}}$  species of vapor particles. It must also be equal to the desorption rate  $E_i$  of the  $i^{\text{th}}$  species, because it is experimentally established that the condensation coefficient equals unity. Hence, eq. (3) can be rewritten as:

$$E_i = \omega_i \sigma_f \theta v \exp(\Delta S/k) \exp(-\phi_i/kT) (\text{cm}^{-2} \text{sec}^{-1}). \quad (4)$$

Clearly, the desorption rate  $E_i$  is derived under the special requirement that the vapor and surface phases be in thermal equilibrium.

### 2.3. DESORPTION RATES OF ATOMS AND IONS

In adsorption systems of interest, a metallic surface is kept at a temperature  $T$  and is immersed in a vapor bath which is maintained, by a liquid reservoir, at a temperature  $T'$  usually less than  $T$ . If it is assumed that eq. (4) is also applicable to these systems, then the desorption rates  $E_a$  of atoms and  $E_p$  of

atoms and  $E_p$  of ions are:

$$E_a = \omega_a \sigma_f \theta v \exp(\Delta S/k) \exp(-\phi_a/kT), \quad (5)$$

$$E_p = \omega_p \sigma_f \theta v \exp(\Delta S/k) \exp(-\phi_p/kT). \quad (6)$$

The desorption energies  $\phi_a$ ,  $\phi_p$  have already been calculated theoretically<sup>2)</sup>. The statistical weights  $\omega_a$ ,  $\omega_p$  and the atom surface density  $\sigma_f$  defined at  $\theta = 1$  are characteristic physical constants of the adsorption system. Hence, the completion of the calculation of  $E_a$  and  $E_p$  requires the explicit computation of the vibrational frequency  $\nu_1$  and the free area  $A_f$ .

### 2.3.1. Calculation of $\nu_1$

There is no exact theory by means of which  $\nu_1$  can be computed in terms of basic quantities. For lack of better information, it is proposed to consider the surface molecules as harmonic oscillators and thus compute the vibrational frequency from the relation:

$$\nu_1 = (1/2\pi)(K/\bar{m})^{\frac{1}{2}} \quad (7)$$

where  $\bar{m}$  the reduced mass and  $K$  the stiffness of the oscillator. This idea has been used by Slater<sup>16)</sup> in calculating unimolecular dissociation rates.

The reduced mass,  $\bar{m}$ , is derived by assuming that the adsorbed particles of mass  $m_f$ , are nestled on top of four substrate particles, each of mass  $m_m$ . This model has already been used<sup>1, 2)</sup>. Thus:

$$\bar{m} = 4m_f m_m / (m_f + 4m_m). \quad (8)$$

Note that a similar but slightly different reduced mass would have been derived if the adsorbate particles were nestled on a different number of substrate particles.

The stiffness,  $K$ , is derived by assuming that the energy of the harmonic oscillator is equal to  $\phi_a$  and that the amplitude of the oscillation, until the bond is ruptured, is equal to  $R \cos \beta$ , namely the thickness of the surface double layer<sup>1)</sup>. Thus:

$$K = \frac{2\phi_a}{(R \cos \beta)^2}, \quad (9)$$

$$\nu_1 = (1/2\pi R \cos \beta) \cdot [\phi_a (m_f + 4m_m) / 2m_f m_m]^{\frac{1}{2}}. \quad (10)$$

Numerical computations of  $\nu_1$  and the effective vibrational frequency  $\nu$  indicate that both  $\nu_1$  and  $\nu$  are very weak functions of  $\phi_a$ ,  $\bar{m}$  and  $\theta$ . A typical calculation is shown in table 1 for Cs on W. The difference between  $\nu$  and  $\nu_1$  is in most instances negligible, and it is in fact always zero at  $\theta = 0$  and  $\theta = 1$ .

### 2.3.2. Calculation of $A_f$

Two simple models have been proposed for the calculation of the free area. These can be classified as the Van der Waals and the cage models.

The Van der Waals model, originally derived for dilute gases, presumes that the adsorbed particles act as rigid billiard balls and encounter only two body collisions. Thus the free area is found to be:

$$A_f = A_t(1 - \gamma_1\theta) \quad (11)$$

where  $\gamma_1$  is a factor with a theoretical value greater than unity. Tompkins<sup>4</sup>) takes  $\gamma_1 = 2$ . This value is not applicable for  $\theta > 0.5$ , however, because then  $A_f$  would be negative. Warner<sup>5</sup>) and Hill<sup>17</sup>) use  $\gamma_1 = 1$  and hence overestimate  $A_f$  for small values of  $\theta$ .

The cage model, originally derived for very dense gases<sup>18</sup>), presumes that a test particle is confined to move in a cage defined by its nearest neighbors. Thus, the free area is found to be:

$$A_f = A_t\gamma_2(1 - \theta^{\frac{1}{2}})^2 \quad (12)$$

where  $\gamma_2$  is a factor with a theoretical value also greater than unity and for a two dimensional square lattice it is equal to  $\pi$ . It is evident that eq. (12) is not satisfactory for all values of  $\theta$  because, for  $\theta > (1 - \gamma_2^{-\frac{1}{2}})^2$ ,  $A_f > A_t$ . If  $\gamma_2$  were taken equal to unity, then eq. (12) would underestimate the value of  $A_f$  for large values of  $\theta$ .

In order to overcome the inherent difficulties of either of eqs. (11) or (12), it is proposed to assume that the free area is given by the geometric mean of the over- and underestimates of the Van der Waals and cage models with  $\gamma_1 = \gamma_2 = 1$ . Thus:

$$A_f = A_t(1 - \theta)^{\frac{1}{2}}(1 - \theta^{\frac{1}{2}}). \quad (13)$$

The ratio  $A_t/A_f$  appears in the desorption rate equations through  $\Delta S$ . The latter quantity may be illustratively and conveniently interpreted as a configuration entropy change because when the particle is desorbed, the number of available configuration complexions is increased.

Numerically the factor  $\exp(\Delta S/k)$  is equal to unity at  $\theta = 0$ , it is about 100 for  $\theta \sim 0.6$  and it becomes very large for  $\theta \sim 1$ . Admittedly, the developed formalism is not applicable for  $\theta$  close to unity. The reason is that before the first adsorbed layer is completed, a second layer starts building up, thus affecting the configuration entropy change. This subject is discussed in greater detail in appendix A.

## 2.4. PRACTICAL REFORMULATION OF DESORPTION RATES

The derived desorption rates may be expressed in forms that are convenient for comparisons between theory and experiment.

Specifically:

$$\log E_a = A_a - 5050\phi_a/T, \quad (14)$$

$$\log E_p = A_p - 5050\phi_p/T, \quad (15)$$

where

$$A_a = \log [\omega_a \sigma_f \theta v \exp(\Delta S/k)], \quad (16)$$

$$A_p = \log [\omega_p \sigma_f \theta v \exp(\Delta S/k)]. \quad (17)$$

In eqs. (14) and (15), rates are in particles/cm<sup>2</sup>/sec, energies in eV, temperature in °K, and logs to the base 10. Note that  $A_a$  and  $A_p$  are dependent on coverage, not temperature explicitly.

### 3. Comparison of theory with reported experimental results

#### 3.1. THE SAHA-LANGMUIR EQUATION

The derived desorption rates are consistent with the well-known and experimentally verified Saha-Langmuir equation. Indeed the ratio of eqs. (5) and (6) yields:

$$E_p/E_a = (\omega_p/\omega_a) \exp[(\phi_e - V_f)/kT] \quad (18)$$

since  $\phi_p = \phi_a - \phi_e + V_f$ , where  $\phi_e$  the surface electron work function and  $V_f$  the adsorbate ionization potential<sup>2)</sup>.

The Saha-Langmuir equation cannot be as readily derived when the adsorbed particles are assumed to be of two distinct species<sup>5,6,8)</sup>. In this case, the derivation requires a complicated energy diagram and an additional assumption regarding the ratio of "adsorbed atoms" to "adsorbed ions".

#### 3.2. EXPERIMENTAL DATA FOR CESIUM ON TUNGSTEN

Taylor and Langmuir<sup>7)</sup> have studied experimentally the properties of a polycrystalline tungsten surface immersed in a cesium vapor. The comparison of the experimental and theoretical values of  $\phi_e$ ,  $\phi_a$ ,  $\phi_p$  is given elsewhere<sup>1,2)</sup>. Hence, in order to compare the measured desorption rates with the rates derived in this paper it is adequate to compare the experimental values of  $A_a$  and  $A_p$  with the values calculated by means of eqs. (16) and (17). The measured values of  $A_a$  for  $\phi < 0.95$  are shown in fig. 1 (circles). Values were not reported for  $\theta > 0.95$ . Superimposed on the figure (solid line) and tabulated in table 1 are also theoretical values of  $A_a$ , calculated by means of eqs. (16) for  $\omega_a = 2$  and  $\sigma_f = 4.8 \times 10^{14}/\text{cm}^2$  (as measured by Taylor and Langmuir). The agreement between theory and experiment for  $\theta < 0.95$  is very good.

It is recognized that the good agreement between experimental and theoretical values of  $A_a$  may be somewhat fortuitous in view of the uncertainties inherent in the calculation of  $\nu_i$  and  $A_f$ . It is believed, however, that the

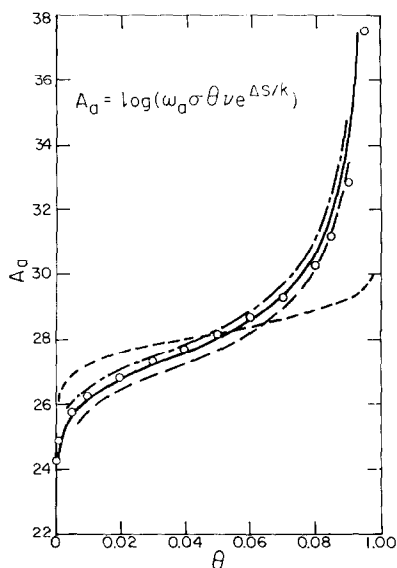


Fig. 1. Comparison of theoretical Arrhenius coefficient  $A_a$  for Cs on W (solid curve) with experimental Taylor-Langmuir data (circles). Uncertainty limits ( $\pm 3\%$ ) inherent in  $A_a$  are shown by the dashed lines. Theoretical values of  $A_a$  based on an immobile model (dotted curve) are also included to show that they do not correlate the data.

TABLE 1

Theoretically calculated data for desorption rates from cesiated tungsten  
( $\sigma_t = 4.8 \times 10^{14}$  atoms/cm<sup>2</sup>)

$\theta$	$\log \nu$ (sec <sup>-1</sup> )	$\Delta S/k^*$	$A_a$ (cm <sup>-2</sup> sec <sup>-1</sup> )	$A_p$ (cm <sup>-2</sup> sec <sup>-1</sup> )
10 <sup>-5</sup>	12.03	0.00	22.01	21.71
10 <sup>-3</sup>	12.03	0.05	24.03	23.73
0.02	12.03	0.32	25.45	23.15
0.1	12.01	0.71	26.30	25.00
0.2	12.00	1.24	26.82	26.52
0.3	11.98	1.80	27.22	26.92
0.4	11.96	2.44	27.60	27.30
0.5	11.95	3.29	28.06	27.76
0.6	11.93	4.48	28.64	28.34
0.7	11.93	6.23	29.46	29.16
0.8	11.92	9.06	30.74	30.44
0.9	11.92	17.69	34.55	34.25
1.0	—	—	—	—

\* In the context of the proposed form for the free area (eq. (13)),  $\Delta S/k$  is independent of material properties.



mobile one species model does reflect the essential features of the physical system. If, for example, a model with *immobile* adsorbed particles had been assumed, each particle having three degrees of vibrational freedom, then the derived expression for  $A_a$  would be:

$$A_a(\text{immobile}) = \log [2\pi\omega_a m_f v^3 \theta / kT (1 - \theta)]. \quad (19)$$

This quantity is plotted in fig. 1 (dashed line), for  $T = 1000^\circ\text{K}$  and  $\nu = 10^{12} \text{ sec}^{-1}$ . The correlation between the experimental data and  $A_a(\text{immobile})$  is unquestionably poor and even if  $T$  were varied by a factor of two the result would not improve.

It is also recognized that eq. (16) is not applicable for  $\theta$  very close to unity, because for  $\theta = 1$ ,  $A_a \rightarrow \infty$ . This is due to the fact that the formalism does not reflect the buildup of the second layer before the completion of the first. An analysis of this effect, described in appendix A, indicates that the second layer transition is sharp and that  $A_a$  should not become infinite. For two or more monolayers, it should reach a finite value characteristic of a liquid surface.

Taylor and Langmuir calculate  $A_p$  in terms of  $A_a$  through the relationship

$$A_p = A_a + \log(\omega_p/\omega_a). \quad (20)$$

Thus, no further information is gained by comparing the Taylor and Langmuir  $A_p$  values with those calculated by means of eq. (17).

For completeness, a series of theoretical isotherms for Cs on W are plotted in fig. 2. These isotherms are representative of all systems for which the bare

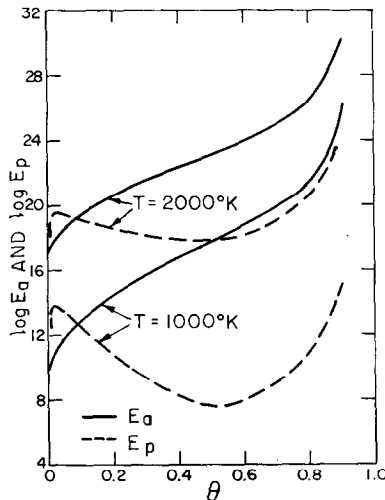


Fig. 2. Theoretical atom desorption rates  $E_a$  and ion desorption rates  $E_p$  of cesium from tungsten plotted versus  $\theta$  at  $T = 1000^\circ\text{K}$  and  $T = 2000^\circ\text{K}$ . Input parameters are characteristic of the Taylor-Langmuir surface; no adjustable constants are used.

substrate electron work function  $\phi_m > V_f$ . They are included to show that atom and ion desorption rates can be explicitly calculated for intermetallic composite surfaces without any adjustable constants.

### 3.3. ELECTRON EMISSION DATA

Theoretical electron emission  $S$  curves can be constructed by combining the values of  $A_a$  calculated by means of eq. (16), the values of  $\phi_a$  as derived in ref. 2), the values  $\phi_o$  given in ref. 1) and known arrival rates of the adsorbate. Such  $S$  curves are presented in part III and compared with experimental results for many substrate and adsorbate combinations. Good agreement between theory and experiment is established which gives additional but indirect evidence that the values  $A_a$  calculated by means of eq. (16) are fairly accurate.

### 3.4. ATOM AND ION LIFETIME DATA

Atom lifetimes,  $\tau_a$ , and ion lifetimes,  $\tau_p$ , can be defined as:

$$\tau_a = \sigma_f \theta / E_a; \quad \tau_p = \sigma_f \theta / E_p. \quad (21)$$

For low coverages ( $\theta \sim 0$ ), eq. (21) combined with eqs. (5) and (6) yields

$$\tau_{a0} = \tau_a^* \exp(\phi_{a0}/kT), \quad \tau_{p0} = \tau_p^* \exp(\phi_{p0}/kT), \quad (22)$$

$$\tau_a^* = 1/\omega_a \nu, \quad \tau_p^* = 1/\omega_p \nu. \quad (23)$$

Comparisons of theoretical and experimental values of initial desorption energies,  $\phi_{i0}$ , have been reported in ref. 2).

Many investigators have correctly presumed that  $\tau_i^*$  is proportional to  $\nu^{-1}$ . They have not, however, recognized the dependence on the statistical weight  $\omega_i$ . For example, for rubidium  $\tau_a^*/\tau_p^* = \omega_p/\omega_a = \frac{1}{2}$  and Hughes and Levinstein<sup>19</sup>) report an experimental ratio smaller than unity. The experimental uncertainties are such as to preclude a more accurate comparison. In general, the dependence of  $\tau_i^*$  on the statistical weight has not yet been clearly verified experimentally.

When vibrational frequencies are calculated by means of eq. (10), absolute values of  $\tau_a^*$  and  $\tau_p^*$  can be derived for a variety of adsorption systems. For example, for the systems Cs-W, Cs-Re, Rb-W and Ba-Re, the theoretical values of  $\tau_p^*$  are 0.9, 0.9, 0.7 and  $0.3 \times 10^{-12}$  sec, respectively. These are to be compared with the corresponding experimental values 1.1, 0.2, 0.3 and  $0.06 \times 10^{-12}$  sec, reported by Hughes and Levinstein<sup>19</sup>) and Scheer and Fine<sup>20</sup>). The numerical disagreement may be due to errors in experimental measurements (log  $\tau_p^*$  is measured and not  $\tau_p^*$  itself), to uncertainties in the calculation of  $\nu$  and to the possibility of surface contamination. It is reported that surface contamination may alter  $\tau_{p0}$  by an order of magnitude<sup>19, 20</sup>).

### 3.5. OTHER EXPERIMENTAL DATA

There are other experimental data, pertinent to desorption rates, that have been reported in the literature. These data, however, cannot be compared with any theory because they are given either without specification of the experimental conditions or in a processed form that does not permit the recovery of the original and meaningful results.

For example, many workers, such as Becker<sup>6)</sup> and Zingerman<sup>12)</sup> report their data without stating explicitly the prevailing experimental conditions. In addition, these authors do not recognize the importance of the configuration entropy change which should be considered in any determination of desorption energies from desorption rates<sup>21)</sup>, especially for  $\theta > 0.1$ .

Other workers, such as Danforth<sup>22)</sup> and Moore and Allison<sup>11)</sup>, do not measure  $\theta$  directly but as a function of time. They make several simplifying assumptions regarding  $A_a$  and  $\phi_a$ , integrate eq. (14) with respect to time and fit certain adjustable constants to experimental data. Consequently, it is not practical to compare the "experimental" values  $A_a$  and  $A_p$  reported by these workers with the theoretical values derived in this paper.

Bosworth<sup>23)</sup> reports data for Na on polycrystalline W, from which  $A_a$  may be calculated. It is found that  $A_a$  decreases slightly with increasing  $\theta$  instead of increasing as the theory predicts. The disagreement may be due to the questionable cross plotting used by Bosworth or to contamination. The reason for questioning Bosworth's procedures is that the initial heat of desorption derivable from his data is only about  $\frac{1}{2}$  of that reported more recently by Starodubtsev<sup>24)</sup> for Na on polycrystalline W.

## 4. Vaporization and sublimation rates from pure surfaces

### 4.1. GENERAL REMARKS

The statistical mechanics formalism developed in sec. 2 can be easily adapted to the problem of calculation of vaporization and sublimation rates of pure substances. Admittedly, these rates can be readily expressed in terms of the vapor pressure and temperature of the system. The adaptation of the statistical mechanics formalism, however, serves several purposes. It avails the derived rate equations with a greater variety of experimental data for comparisons and it provides directly analogous expressions for desorption and vaporization rates. The latter aspect is very useful in part III where simple state functions for composite surfaces are formulated.

### 4.2. VAPORIZATION RATES

The model chosen for the calculation of vaporization rates is a monatomic

liquid surface phase at temperature  $T'$  in thermal equilibrium with its own vapor\*. It is assumed that when a particle is emitted from the surface, its vacancy is immediately filled by another particle of the bulk liquid. Thus the number of surface particles  $N'$  is constant. Also, it is assumed that the liquid particles on the surface are fully mobile since they are not restricted to a precise plane. Thus the free area is taken equal to the total area,  $A_f = A_t$ , resulting in a configuration entropy change equal to zero.

The interpretation of the general eq. (4) in terms of the stated particulars of the vaporization model indicates that the vaporization rate  $E'$  is:

$$E' = \omega'_a \sigma' v' \exp(-\phi'/kT'), \quad (24)$$

where  $\omega'_a$  = the statistical weight of the vapor,

$\sigma'$  = the surface density of the liquid particles,

$v'$  = the vibrational frequency of the liquid particles,

$\phi'$  = the potential energy of vaporization.

#### 4.2.1. Calculation of $\sigma'$

The surface density cannot be directly determined because of the chaotic motion of the particles of the vaporizing liquid surface. A reasonable estimate can be made, however, by assuming that  $\sigma'$  is equal to the two thirds power of the particle volume density in the interior of the liquid<sup>26</sup>). Computed values of  $\sigma'$  for all the alkali metals are given in table 2. It is expected that these densities may have an inherent uncertainty of about 25% and no attempt is made to account for thermal expansion effects.

#### 4.2.2. Calculation of $v'$

Because of the random motions of the liquid particles, the vibrational frequency also cannot be unambiguously determined. Nevertheless, a reasonable estimate can be derived by assuming  $v'$  equal to the vibrational frequency of the diatomic molecule in the vapor phase whenever this is possible.

TABLE 2  
Calculated vaporization and sublimation parameters of alkali metals

Elements	$\sigma'$ (cm <sup>-2</sup> )	$v'$ (sec <sup>-1</sup> )	$A'$ (cm <sup>-2</sup> sec <sup>-1</sup> )	$\phi'$ (eV)	$A''$ (cm <sup>-2</sup> sec <sup>-1</sup> )	$\phi''$ (eV)
Cs	$4.16 \times 10^{14}$	$1.26 \times 10^{12}$	27.02	0.747	27.45	0.773
Rb	$1.90 \times 10^{14}$	$1.72 \times 10^{12}$	27.23	0.792	27.66	0.819
K	$5.63 \times 10^{14}$	$2.78 \times 10^{12}$	27.50	0.862	27.93	0.928
Na	$8.73 \times 10^{14}$	$4.77 \times 10^{12}$	27.92	1.236	28.35	1.310
Li	$12.90 \times 10^{14}$	$10.54 \times 10^{12}$	28.43	1.556	28.86	1.647

\* This model is different from the models reviewed by Fowler and Guggenheim<sup>25</sup>) in which the two phases are the liquid interior and the vapor.

Diatomic molecule frequencies can be measured spectroscopically<sup>27)</sup> and are tabulated in table 2 for all the alkali metals.

#### 4.2.3. Sublimation rates

Sublimation rates can be calculated in terms of the vaporization rates by considering the melting transition. A statistical mechanics analysis, reviewed by Fowler and Guggenheim<sup>28)</sup>, shows that the change in entropy of melting  $\Delta S_M$  is approximately equal to the Boltzmann constant  $k$ . Thus, sublimation rates are calculated to be:

$$E'' = \omega_a \sigma' v' e \cdot \exp [ - (\phi' + kT_M) / kT' ]. \quad (25)$$

### 5. Comparison of vaporization theory with reported experimental results

Consider first the cesium system. Vaporization rates have been quoted by Houston<sup>29)</sup> and are shown as circles in fig. 3. Sublimation rates are quoted by Taylor and Langmuir<sup>7)</sup> and are also shown in fig. 3 as crosses.

Superimposed on the same figure are values predicted theoretically by means of table 2, and eqs. (24–25). The agreement between theory and experiment is good over the temperature range  $250^\circ < T' < 600^\circ\text{K}$ . Admittedly, this agreement may be somewhat fortuitous since  $\sigma'$  and  $v'$  are not accurately known.  $\phi'$  is close to the reported heat of vaporization.

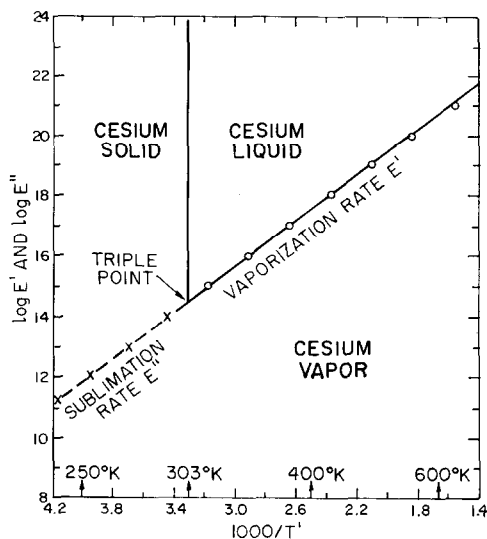


Fig. 3. Comparison of theoretical values of cesium vaporization rate  $E'$  and cesium sublimation rate  $E''$  (straight lines) with experimental values (circles and crosses). Note slight discontinuity in slopes at triple point.

Vaporization and sublimation rates for other alkali metals are not quoted in the literature directly as functions of temperature. These rates, however, may be calculated from vapor pressure data quoted by Smithells<sup>30)</sup> by means of the equation:

$$E' = p (2\pi mkT')^{-1/2}. \quad (26)$$

The great bulk of Smithells' information is in the vaporization region and is depicted in fig. 4 for Rb, K, Na and Li. Superimposed on the same figure are also the theoretical predictions calculated by means of eq. (24). The agreement

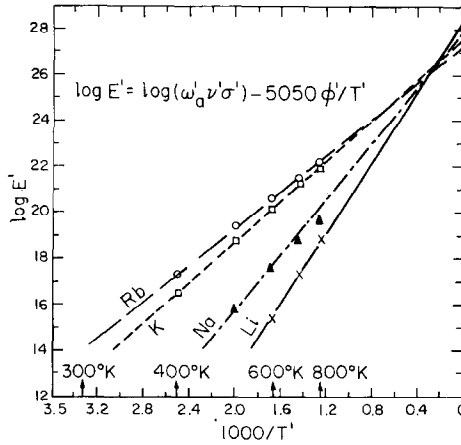


Fig. 4. Comparison of theoretical values of vaporization rates  $E'$  (straight lines) with experimental values for Rb (circles), K (squares), Na (triangles) and Li (crosses).

between theory and experiment for Rb, K, and Li is better than  $\frac{1}{2}\%$  in the temperature range 300–800°K. The agreement is not so good for Na. The reason for the discrepancy is not understood. Note that the intercept is fixed at  $A'$  as calculated from table 2.

## 6. Conclusions

For the particular system of monatomic metallic particles adsorbed on metals, desorption rates of atoms and ions have been calculated theoretically. They are expressed as functions of coverage, surface temperature and basic physical parameters by means of statistical mechanics. The derived equations are unique in the respect that no adjustable constants need be used, and in that they have a large range of applicability. They apply to all coverages ( $0 < \theta \lesssim 1$ ) where the second layer complication does not appear, and they apply to all combinations of monatomic metallic films adsorbed on all metals. Two important terms arise from the statistical mechanics analysis

which have not been stressed by others. They are the statistical weight and the configuration entropy difference. A similar statistical mechanics analysis applied to vaporization shows the close analogy between desorption and vaporization processes and shows the generality of the method. Comparison of theory with available experimental data is very good.

If different substrate properties cause different adsorbate patches to exist on a surface, these patches will have identical desorption rates but different coverages. Diffusion between these patches is not necessary to establish equilibrium and the proposed desorption theory can be applied to each homogeneous patch individually.

The small but complicating effects of thermal expansions have not been included in the calculations. As a result of this omission,  $A_a$ ,  $A_p$  and  $A'$  do not depend on temperature. Also the effects of the formation of a second layer, before the completion of the first, are not included. An approximate calculation of these effects is given in the appendix.

## Appendix A

### SECOND LAYER ANALYSIS

The purpose of the appendix is to calculate approximately the temperature conditions for which the second layer becomes important. Thus the range of applicability of the equations derived in the text will be clearly defined.

To this end, let  $N_2$  be the number of adsorbed particles in the second layer,  $N_1$  be the number of adsorbed particles in the first layer and  $N_m$  the total number of adsorbed particles corresponding to one monolayer. Consider the case where  $N_2 \ll N_m$  and  $N_1 \sim N_m$ . Assuming that the atom desorption energy from the second layer is  $\phi'$ , that the vibrational frequency is the same for particles of either layer and that the free area of the  $N_2$  particles is  $A_t$  because  $N_2 \ll N_m$  (see eq. (13)), it is found that:

$$N_2/N_1 = \exp(\Delta S/k) \exp[(\phi' - \phi_a)/kT]. \quad (\text{A1})$$

When the arrival rate of vapor particles (eq. (24)) is equated to the desorption rate for  $\theta \sim 1$  (eq. (5)), without the perturbation of the second layer, it is found that:

$$\Delta S/k \simeq \phi_a/kT - \phi'/kT' \quad (\text{A2})$$

where  $T'$  is the vapor temperature.

Combination of eqs. (A1) and (A2) yields:

$$N_2/N_1 \cong \exp(-\Delta T/T_s) \quad (\text{A3})$$

where  $\Delta T = T - T'$  and  $T_s = kT'^2/\phi'$ .

The meaning of eq. (A3) is that for  $\Delta T \gg T_s$  the second layer buildup is unimportant and the equations derived in the text are applicable. To illustrate the point numerically, consider cesium as an adsorbate. For  $\phi' = 0.8$  eV,  $T' = 270^\circ\text{K}$ ,  $T_s$  becomes  $8^\circ\text{K}$ . This small value of  $T_s$  indicates that, for cesium on metals, the transition from the first to the second layer occurs over a very narrow temperature range near the vapor bath temperature. The transition is sharp and easily observed experimentally. Taylor and Langmuir<sup>7</sup> measured  $N (= N_1 + N_2)$  versus  $T$  and they find that the transition is sharp. In fact, from the Taylor and Langmuir data it can be inferred that at  $T' = 270^\circ\text{K}$ ,  $T_s = 8^\circ\text{K}$ , a result that is in agreement with the present analysis. Similar experimental observations of the sharp transition to the second layer have been reported by others<sup>11,31</sup>.

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